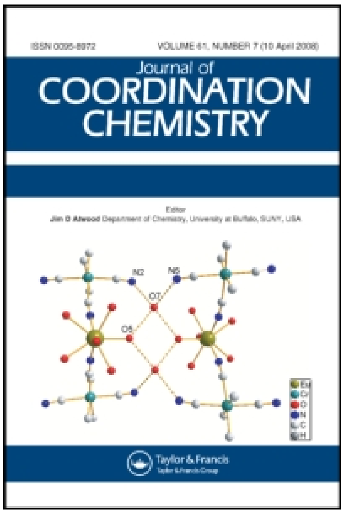

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

STUDIES ON MIXED LIGAND COMPLEXES, PART II. COBALT(III) HETEROCHELATES CONTAINING NONPLANAR QUADRIDENTATE LIGANDS

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To cite this Article Syamal, A. and Ghanekar, V. D.(1975) 'STUDIES ON MIXED LIGAND COMPLEXES, PART II. COBALT(III) HETEROCHELATES CONTAINING NONPLANAR QUADRIDENTATE LIGANDS', Journal of Coordination Chemistry, 5: 1, 39 — 44
To link to this Article: DOI: 10.1080/00958977508075917
URL: http://dx.doi.org/10.1080/00958977508075917

J. Coord. Chem.
1975, Vol. 5, pp. 39–44.

STUDIES ON MIXED LIGAND COMPLEXES, PART II. COBALT(III) HETEROCHELATES CONTAINING NONPLANAR QUADRIDENTATE LIGANDS

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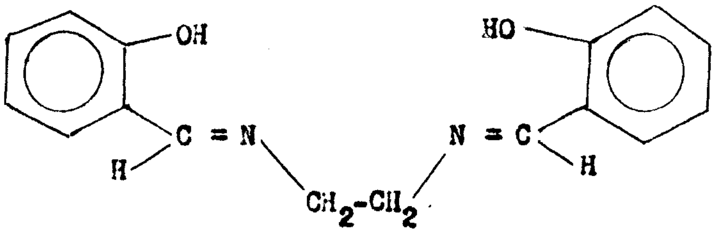
(*Received January 30, 1975; in final form May 19, 1975*)

A series of new cobalt (III) mixed ligand complexes of the type [Co(AA) (BBBB)] [where AA = bidentate monobasic NO or OO donor ligands such as picolinic acid, quinaldinic acid, acetylacetone, tropolone, acetoacetanilide, N-benzoylphenylhydroxylamine, benzohydroxamic acid, and BBBB = quadridentate ONNO donor ligand like N,N'-trimethylenediaminebis (salicylideneimne)(saltnH$_2$)] were synthesized and characterized by elemental analysis, conductance measurements, electronic spectra, infrared spectra, molecular weight and magnetic susceptibility measurements. The complexes are green in color, monomers, non-electrolytes and diamagnetic. In these heterochelates the quadridentate ligand saltn adopts an unusual nonplanar twisted conformation and the bidentate ligand occupies two *cis* positions. The magnetic and electronic spectral data of the complexes indicate distorted octahedral structure of the complexes. Electronic spectral data in non-coordinating and coordinating solvents indicate that the heterochelates with saltn are stable to pyridine attack which is contrary to the electronic spectra of similar heterochelates with salen [where salenH$_2$ = N,N'-ethylenediaminebis (salicylideneimine)]. The latter heterochelates undergo rearrangement in pyridine and two molecules of pyridine enter the coordination zone with simultaneous removal of the bidentate ligand.

INTRODUCTION

The cobalt (III) complexes containing quadridentate dibasic ONNO donor ligand salenH$_2$(I) and various bidentate ligands have been the object of considerable interest[2-6]. The structures of some of these complexes (II) have been determined by single crystal X-ray[3,6]. NMR and molecular weight studies indicate that the structures of the complexes in both solid state and solution are same. The complexes II with salen undergo rearrangement in pyridine indicating the presence of strain due to the non-planar coordination of salen[5]. In complexes II with saltn it is expected that the strain will be less in comparison to salen complexes due to the chelate ring effect. We thought it worthwhile to test the stability of complexes II with saltn in pyridine. In this article we report the syntheses of some new cobalt (III) mixed ligand complexes containing nonplanar Schiff base saltnH$_2$(III) and bidentate NO donor ligands picolinic acid, quinaldinic acid, and bidentate OO donor ligands acetylacetone, tropolone, acetoacetanilide, N-benzoylphenylhydroxylamine and benzohydroxamic acid. The complexes are characterized by elemental



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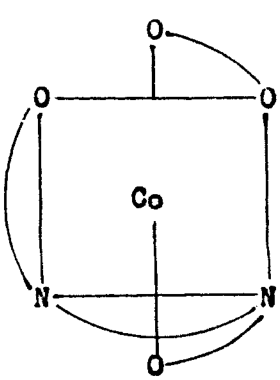

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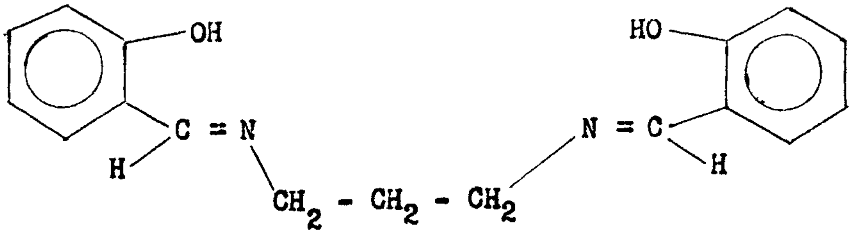


III

analysis, conductance measurements, infrared spectra, electronic spectra, magnetic susceptibility and molecular weight measurements. A comparison of the electronic spectral behavior of [Co(AA)(saltn)] and [Co(AA)(salen)] in pyridine is presented.

EXPERIMENTAL

Materials

Cobalt (II) chloride hexahydrate, acetylacetone, pyridine, nitrobenzene and acetone were BDH analar products. Trimethylenediamine and bromoform were obtained from Fluka AG, Switzerland. Tropolone, acetoacetanilide, N-benzoylphenylhydroxylamine and benzohydroxamic acid were purchased from Aldrich Chemical Co., U.S.A. Salicylaldehyde was procured from Sarabhai M. and Co.

Physical Measurements

Electrolytic conductance measurements were done with the help of a Radelkis type OK 102/1 conductivity bridge and a dip type cell. Molecular weight measurements were done by cryoscopic method of the depression of freezing point in nitrobenzene or the elevation of boiling point in bromoform. Magnetic susceptibility measurements were carried out at room temperature by the Gouy method using Hg [Co(NCS)$_4$] as the calibrant. Infrared spectra were recorded in KBr pellets on a Perkin Elmer Model 21 infrared spectrophotometer. Each spectrum was calibrated with a polystyrene film. Electronic spectra were recorded with the help of a Beckman DK2 recording spectrophotometer using 10 mm matched quartz cells. Carbon, hydrogen and nitrogen analyses were done by the University of Bombay Analytical services and cobalt analyses were done gravimetrically weighing as anhydrous CoSO$_4$. The analytical data of the complexes are presented in Table I.

General Method of Preparation of the Complexes

For complexes with the ligands picolinic acid, quinaldinic acid, tropolone, acetylacetone, acetoacetanilide, and N-benzoylphenylhydroxylamine Co(saltn)^{7a} (1g, 0.003 mole) was suspended in 20–30 ml of absolute alcohol. The appropriate ligand (0.003 mole) was dissolved in 15–20 ml of absolute alcohol and added to the above suspension. The mixture was refluxed on water bath for 1 hr. In case of acetylacetone and acetoacetanilide the refluxion period was 6 hrs. and 1:6 Co(saltn) : ligand ratio was used. After filtration the volume of the filtrate was reduced partially by heating on a water bath. A slow stream of nitrogen helped the evaporation process. The separated green precipitates were suction filtered and washed with alcohol and ether. This crude product was dissolved in minimum amount of 1:1 chloroform:absolute alcohol mixture (acetone for acetoacetanilide complex) and pure compounds were obtained by partial evaporation of the solvents on water bath and subsequent cooling in an ice bath. In case of the quinaldinic acid complex the solvents were partially removed under a fan at room temperature. The complexes were filtered, washed with alcohol followed by ether and dried under vacuum at room temperature. The yield varied from 20–55%.

[Co(benzohydroxamic acid) (saltn)] Co(saltn) (1g, 0.0030 mole) was suspended in 20 ml of acetone. To this an acetone solution of benzohydroxamic acid (0.0030 mole in 20 ml) was added and the mixture was then refluxed for 1 hr. and filtered. The filtrate was partially reduced under a fan at room temperature. The separated green compound was filtered and dissolved in minimum amount of acetone. Partial removal of acetone under a fan at room temperature gave pure product. The compound was suction fil-

TABLE I
Analytical and molar conductance data of cobalt(III) heterochelates

Complex	Stoichiometry	Analytical data								Molar conductance
		Calcd				Found				
		%C	%H	%N	%Co	%C	%H	%N	%Co	ohm^{-1} cm^2 mole^{-1}
[Co(picolinic acid)(saltn)]H_2O	$CoC_{23}H_{22}O_5N_3$	57.62	4.59	8.77	12.32	56.3	5.1	8.7	12.3	1.7
[Co(quinaldinic acid)(saltn)]H_2O	$CoC_{27}H_{24}O_4N_3$	61.25	4.54	7.94	11.15	58.6	4.9	8.1	–	2.5
[Co(acetylacetone)(saltn)]	$CoC_{22}H_{23}O_4N_2$	60.27	5.25	6.39	13.47	60.6	5.5	6.7	13.7	0.7
[Co(tropolone)(saltn)]	$CoC_{24}H_{21}O_4N_2$	62.61	4.57	6.09	12.83	61.9	5.1	5.7	12.6	1.4
[Co(acetoacetanilide)(saltn)]	$CoC_{27}H_{26}O_4N_3$	62.91	5.05	8.16	11.46	61.8	5.6	8.0	11.9	5.0
[Co(benzoylphenylhydroxylamine)(saltn)]	$CoC_{30}H_{26}O_4N_3$	65.34	4.72	7.62	10.71	65.4	4.9	7.9	10.7	0.5
[Co(benzohydroxamic acid(saltn)]	$CoC_{24}H_{21}O_4N_3$	60.76	4.43	8.86	12.45	60.2	4.7	9.1	12.7	4.3

tered, washed with ether and dried under vacuum. Yield = 20%.

RESULTS AND DISCUSSION

The heterochelate complexes were synthesized by reacting the bidentate ligands with Co(saltn) in absolute alcohol or acetone at water bath temperature. The magnetic susceptibility measurements on the synthesized complexes indicate that the complexes are diagmagnetic as expected for d^6 cobalt (III) complexes of octahedral symmetry. Apparently cobalt (II) complex of saltn is oxidised to cobalt (III) under the reaction condition resulting in the formation of six-coordinate heterochelates. The complexes are green in color and are recrystallisable from acetone or 1:1 ethanol:chloroform mixture. The complexes are soluble in a variety of organic solvents such as methanol, ethanol, chloroform, bromoform, dioxane, acetone, benzene, nitrobenzene and pyridine. The complexes behave as non-electrolytes in methanol (Λ_M = 0.4–5.0 ohm^{-1} cm^2 mole^{-1}). We have measured molecular weights of several complexes in nitrobenzene by cryoscopic method and the complexes were found to be monomeric in this solvent. Some molecular weight measurements were also done in bromoform by the same method and similar results were obtained.

Infrared spectral data of the free ligands and the heterochelates in the range 1500–1800 cm^{-1} are given in Table II along with probable band assignments. The ligand saltn has a band at 2650 cm^{-1} due to the intramolecularly hydrogen bonded OH group[7b]. This band disappears in the spectra of the heterochelates indicating the breaking of the hydrogen bond and coordination through the phenolic oxygen atoms. Only in two complexes viz. [Co(picolinic acid) (saltn)] H_2O and [Co(quinaldinic acid) (saltn)] H_2O a new band at 3300 cm^{-1} appears which can be assigned to ν(OH) stretch of water of crystallization as the coordinated water molecules usually exhibit ν(OH) stretch at around 3100 cm^{-1} (ref. 8). In some complexes the ν(C = O) vibrations can be located and these vibrations occur at lower frequencies in comparison to those of the ligand bands which is indicative of oxygen coordination of OO and NO donor bidentate ligands. The ν(C = N) and conjugated phenyl ring vibrations of saltn H_2 shift to higher frequencies in the heterochelate complexes in accordance with the infrared spectra of metal chelates of similar ligands[9].

We have recorded the electronic spectra of the

TABLE II

Infrared spectral data of ligands and cobalt(III) complexes in the region 1500–1800 cm^{-1}

Probable assignments	Saltn H_2	Picolinic acid	[Co(picolinic acid)(saltn)] H_2O	Quinaldinic acid	[Co(quinaldinic acid)(saltn)] H_2O	Acetylacetone
ν(C=O)						1710 s
ν(COO^-)		1690 s	1600 s	1690 s	1612 s	
Amide I						
ν(C=C)	1617 s					1610 s
Conjugated phenyl ring	1585 s		1600 s		1612 s	
ν(C=N)	1500 m	1575 s	1535 m	1577 s	1530 m	
Amide II						

Probable assignments	[Co(acetyl-acetone) (saltn)]	Tropolone	[Co(tropolone) (saltn)]	Acetoaceta-nilide	[Co(acetoace-tanilide) (saltn)]	Benzoylphenyl-hydroxylamine
ν(C=O)	1590 s	1610 s	1595 s	1730 s	1620 s	1630 s
ν(COO^-)						
Amide I				1660 s		
ν(C=C)	1628 s	1550 m	1630 s	1600 s	1620 s	1585 s 1570 s
Conjugated phenyl ring	1590 s		1595 s		1590 s	
ν(C=N)	1510 m		1510 s		1535 s	
Amide II				1540 s		

Probable assignments	[Co(benzoylphenyl-hydroxylamine (saltn)]	Benzohydroxamic acid	[Co(benzohydroxamic acid)(saltn)]
ν(C=O)	1610 m	1642 s	1595 s
ν(COO^-)			
Amide I			
ν(C=C)	1630 s	1612 s	1615 s
Conjugated phenyl ring	1610 m		1595 s
ν(C=N)	1535 s		1540 m
Amide II		1560 s	

All bands are in cm^{-1}.

Abbreviation: s = strong, m = medium.

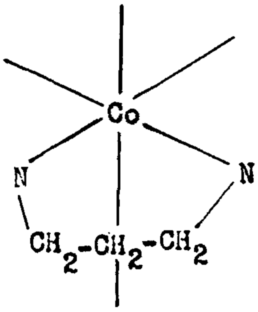
In [Co(acetylacetone)(saltn)], [Co(tropolone)(saltn)], [Co(acetoacetanilide)(saltn)], [Co(benzoylphenylhydroxylamine)(saltn)], and [Co(benzohydroxamic acid)(saltn)] the band at 1510, 1510, 1535, 1535, and 1540 cm^{-1} respectively may also be assigned to the ν(C=C) band due to the bidentate ligands.

TABLE III

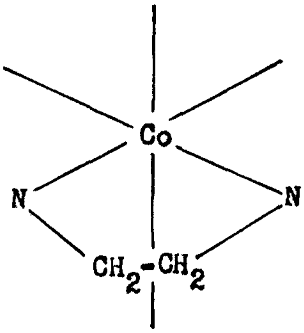
Electronic spectral data of cobalt(III) heterochelates.

Complex	Medium	ν_{max}(log ε)cm^{-1}
[Co(picolinic acid)(saltn)] H_2O	Chloroform	16890 (2.64), 25770 (3.81), 39210 (4.70)
	Pyridine	17000 (2.51), 25710 (3.86)
[Co(quinaldinic acid)(saltn)] H_2O	Chloroform	17040 (2.48), 25640 (3.78), 38910 (4.72)
	Pyridine	17090 (2.50), 25510 (3.88)
[Co(acetylacetone)(saltn)]	Chloroform	16830 (2.53), 26180 (3.83), 39210 (4.81)
	Pyridine	16830 (2.47), 25810 (3.90)
[Co(tropolone)(saltn)]	Chloroform	16720 (2.51), 26250 (4.03), 40400 (4.84)
	Pyridine	16830 (2.45), 26040 (4.16)
[Co(acetoacetanilide)(saltn)]	Chloroform	16670 (2.50), 26180 (3.80), 38910 (4.79)
	Pyridine	16700 (2.43), 25810 (3.87)
[Co(benzoylphenylhydroxylamine)(saltn)]	Chloroform	16950 (2.53), 26670 (3.82), 39220 (4.77)
	Pyridine	17000 (2.52), 26180 (3.88)
[Co(benzohydroxamic acid)(saltn)]	Chloroform	17010 (2.50), 26600 (3.70), 39680 (4.68)
	Pyridine	17030 (2.50), 26320 (3.83)

complexes in both non-coordinating and coordinating solvents and the spectral data are presented in Table III. Octahedral cobalt (III) complexes should have two spin-allowed d-d transitions and exhibit two absorption bands in the visible at around 20000 and 28000 cm^{-1} associated with the transitions $1A_{1g} \rightarrow 1T_{1g}$ (band I) and $1A_{1g} \rightarrow 1T_{2g}$ (band II) respectively. The splitting of band I is usually observed in the low-symmetry complexes due to the splitting of $1T_{1g}$ state to A_2g and Eg states. The complexes reported in this study exhibit two bands at around 16000 and 25000 cm^{-1}. The band at 16000 cm^{-1} may safely be assigned to a d-d transition (band I). A review of electronic spectral bands of a large number of cobalt (III) complexes indicate that the energy difference between the band I and band II is usually 7000–10000 cm^{-1}. Hence the band at 25000 cm^{-1} in our complexes should be assigned to the $1A_{1g} \rightarrow 1T_{2g}$ transition. However the intensity of this band is much higher than what is expected for a d-d transition and we feel this higher intensity is due to the contribution of metal-ligand transitions. The band III at around 40000 cm^{-1} is assigned to charge transfer transitions and/or transitions in the ligand considering the high intensity and position of the band. We have recorded nujol mull spectra of some of our complexes and noticed that the band positions in solid state and chloroform solution occur at comparable energy. This indicates that the structure of the complexes in solid state and chloroform solution is similar. Electronic spectral studies and molecular weight data indicate that the complexes are quite stable in spite of the strain present due to the non-planar conformation of quadridentate Schiff base saltn. To test the stability of the complexes in coordinating solvents we have recorded the electronic spectra of the complexes in pyridine. Quite interesting results have emerged from the spectral studies of the complexes in pyridine. The electronic spectra of the heterochelates with saltn in chloroform and pyridine are quite similar. On the other hand Cummins et al.[5] have noticed that the spectra of [Co(β-diketone) (salen)] in non-coordinating and coordinating solvents are quite different. In the electronic spectra of these complexes in pyridine the intensity of band II increases and band I disappears as it is covered underneath the intense transitions. This spectacular change in the electronic spectra in pyridine has been attributed to the pyridine coordination with the simultaneous removal of the bidentate ligand from the coordination zone[5]. The stability of the heterochelates with saltn in pyridine may be attributed to the chelate ring effect. The complexes with saltn form a six-membered ring around cobalt (III) in the amine part of the complexes. On the other hand salen complexes form a five-membered ring around cobalt (III).



saltn complex



salen complex

The apparent chelate ring effect is the less strain in saltn complexes in comparison to salen complexes. Due to the less strain in saltn complexes, the heterochelates with saltn are stable in pyridine solution. We dissolved [Co(acetoacetanilide) (saltn)] in pyridine and removed pyridine under reduced pressure and dried the compound over silica gel. The green product was dissolved in minimum amount of chloroform and filtered. Addition of petroleum ether (b.p. 40–60°C) to the filtrate produced the original green compound thus verifying the stable nature of the complex in pyridine. It is interesting to note that under similar conditions [Co(OO)(salen)] produces brown complex containing two pyridine molecules in the coordination zone, viz. trans-$[Co(Py)_2 (salen)]^+$ (ref. 5).

ACKNOWLEDGEMENTS

The authors are indebted to the University Grants Commission, New Delhi-1 and the Faculty Research Fund of the University of Bombay for financial support of this research.

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